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# **Molecular Response in One Photon Absorption: Coherent Pulsed Laser vs. Thermal Incoherent Source**

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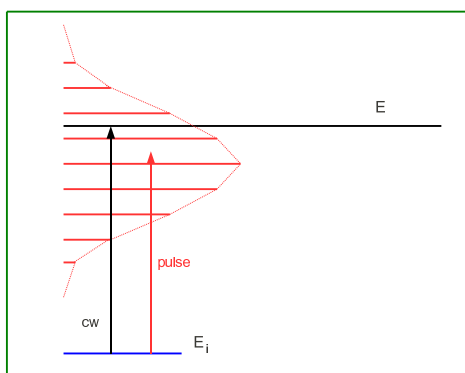
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## Abstract

Photoinduced biological processes occur via one photon absorption in weak incoherent CW light. Here, the nature of molecular dynamics induced by single photon absorption from a pulsed coherent laser source and from an incoherent thermal source of electromagnetic radiation are considered using a quantized radiation field. The former is shown to induce time evolution in the molecule, whereas the latter does not. Confusions in the literature regarding this issue are shown to emerge from a lack of appreciation of (a) the proper description of the absorbed photon and of (b) the role of measurement in understanding the process.

## TOC Image



**Keywords:** Light Harvesting; One-photon absorption; Pulsed coherent light; Incoherent Thermal Light; Quantized Radiation Field

The nature of molecular response to weak electromagnetic fields, where the probability of absorbing a photon is small, is the subject of considerable importance in light-induced biological processes. Examples include light harvesting complexes<sup>1,2</sup> and vision<sup>3</sup>, both of which operate in the domain of weak photon flux.

Of particular concern at present is understanding differences in the molecular response to pulsed coherent laser light used in laboratory laser experiments<sup>4-6</sup> and natural light where the incident radiation arises from a thermal source that is essentially CW and completely incoherent<sup>7,8</sup>. The case where molecules are irradiated with *classical* light has been treated in some detail, leading to the conclusion that isolated molecules subject to pulsed coherent laser light display subsequent time evolution, whereas those subject to incoherent light from a thermal CW source do not<sup>7</sup>. In addition, that study showed that pulsed incoherent light, which by definition is partially coherent, induces time evolution on the time scale of the pulse. i.e. the molecule responds to the time envelope of the light pulse. Hence, for sunlight, for example, the time scale of the dynamics is hours, i.e. there is no dynamics at all on a molecular time scale.

Although recognized, this argument is largely being ignored in applications to weak fields, where the probability of single photon absorption is small due to the low photon flux. For example, a current qualitative description<sup>9</sup> suggests that the absorption of a single photon triggers the same coherent molecular response, regardless of the character of the light source. In particular, a single photon, incident on a molecule, whether arising from a pulsed coherent laser source or from an incoherent CW black body source, is said to induce dynamical evolution. Further, there are related concerns within the community associated with times of arrival of the photons, the role of different bases that can be used to describe the incident light, etc.

This letter, which has two parts, addresses these concerns. In the first part we formulate the problem of one-photon absorption using quantized radiation fields (extensive introductions to the approach used below are provided in Refs.<sup>10,11</sup>. See also Ref.<sup>12</sup>). The quantized radiation field approach allows for consideration of an expanded collection of photon sources, and provides a better focus on the role of the photon itself. This treatment clearly shows that one photon absorption from a pulsed coherent source induces molecular dynamics whereas one photon absorption from an incoherent CW thermal source does not. In the second part, we utilize these results to provide qualitative insight into the nature of the photon,

emphasizing that the description of the photon necessarily carries with it information about the source of the radiation. Problems that have arisen in qualitatively understanding this process are shown to arise from an elementary view of the particulate nature of the incident light. Further, a discussion in terms of the role of measurement in understanding these issues is provided.

We emphasize that considerations below apply to an isolated system. Open systems coupled to an environment are discussed elsewhere<sup>8,13</sup>.

Consider the interaction of a radiation with an isolated material system that is initially in a stationary state  $|E_i\rangle$ . For notational convenience this state is assumed non-energetically degenerate. Higher eigenstates of energy  $E_j$  are denoted  $|E_j, \mathbf{m}\rangle$ , where  $\mathbf{m}$  denotes any additional quantum numbers needed to describe the state. States of the radiation field are written below in terms of number states  $|N_k\rangle$ . Here  $N_k$  is the number of photons in the  $k^{\text{th}}$  mode, of frequency  $\omega_k$ , and  $k = 1, \dots, N$  is a (plane wave) mode index.

Consider now absorption from an arbitrary coherent pulse of light. A general pulse of this kind, linearly polarized along the  $\hat{e}$  direction, can be parametrized as a sum of superpositions of products of number states  $|N_i\rangle$ :

$$|R_i\rangle = \hat{e} \sum_{N_1, N_2, \dots, N_{max}} c(N_1, N_2, \dots, N_{max}) |N_1\rangle |N_2\rangle \dots |N_{max}\rangle, \quad (1)$$

For computational simplicity we also use the notation

$$|R_i\rangle = \hat{e} \sum_{\mathbf{N}} c(\mathbf{N}) |\mathbf{N}\rangle. \quad (2)$$

where  $\mathbf{N} = (N_1, N_2, \dots, N_{max})$ .

For example, output from a standard multi-mode laser source can be well represented as a product  $|R_i\rangle = \prod_k |\alpha_k\rangle$  of coherent states  $|\alpha_k\rangle$ , where<sup>10,14</sup>

$$|\alpha_k\rangle = \exp(-|\alpha_k|^2/2) \sum_{N_k} \frac{\alpha_k^{N_k}}{(N_k!)^{1/2}} |N_k\rangle, \quad (3)$$

i.e.,

$$c(N_1, N_2, \dots, N_{max}) = \prod_{k=1}^{N_{max}} \exp(-|\alpha_k|^2/2) \frac{\alpha_k^{N_k}}{(N_k!)^{1/2}} \quad (4)$$

The larger the parameter  $\alpha_k$ , the closer the radiation is to classical light.

Consider then the interaction of a general pulse with an isolated material system that is initially in a stationary state  $|E_i\rangle$ . The initial radiation-matter state is then given by

$$|\Psi_i\rangle = |R_i\rangle |E_i\rangle. \quad (5)$$

Assuming the dipole approximation and using first order perturbation theory, the final state, after absorbing *one photon* from the above pulse, becomes a radiation-matter wave packet, in the excited state, of the form

$$|\Psi_f\rangle = \frac{2\pi i \hat{\epsilon}}{\hbar} \sum_k \sum_{\mathbf{m}} \varepsilon(N_k, \omega_k) |E_k, \mathbf{m}\rangle \langle E_k, \mathbf{m} | \hat{\epsilon} \cdot \mathbf{d} | E_i \rangle \times \sum_{\mathbf{N}} c(\mathbf{N}) |N_1\rangle \dots |N_{k-1}\rangle |N_k - 1\rangle |N_{k+1}\rangle \dots |N_{max}\rangle, \quad (6)$$

Here  $\mathbf{d}$  is the electric dipole operator and  $E_k = E_i + \hbar\omega_k$  is the energy imparted to the material system as a result of the absorption of one photon of frequency  $\omega_k$ . The field amplitude  $\varepsilon(N_k, \omega_k)$  introduced above is defined as

$$\varepsilon(N_k, \omega_k) = i \left( \frac{\hbar\omega_k N_k}{\epsilon_0 V} \right)^{\frac{1}{2}} \exp(i\omega_k z/c), \quad (7)$$

with  $z$  denoting the axis of propagation of the light beam,  $\epsilon_0$  is the permittivity of the vacuum, and  $V$  is the cavity volume. Note that the resultant state [Eq. (6)] is an entangled superposition of the states of the molecule and the radiation field.

Our interest lies in the state of the system, as opposed to the state of the (system + radiation field). In accord with standard quantum mechanics<sup>15</sup>, one extracts this information from  $|\Psi_f\rangle$  by constructing the density matrix  $|\Psi_f\rangle\langle\Psi_f|$  and tracing over the radiation field to give the density matrix of the molecule, denoted  $\rho_{mol}$ . Doing so, gives:

$$\begin{aligned} \rho_{mol} &= \sum_{\mathbf{N}'} \langle \mathbf{N}' | \Psi_f \rangle \langle \Psi_f | \mathbf{N}' \rangle \\ &= \sum_{\mathbf{N}, \mathbf{m}, \mathbf{m}', k} |c(\mathbf{N})|^2 |A(k, \mathbf{m})\rangle \langle A(k, \mathbf{m}')| + \sum_{\mathbf{N}, \mathbf{m}, \mathbf{m}', k' > k} [d_{k', k} |A(k, \mathbf{m})\rangle \langle A(k', \mathbf{m}')| + cc] \end{aligned} \quad (8)$$

where  $cc$  denotes the complex conjugate of the term that precedes it,

$$d_{k', k} = c(N_1, N_2, \dots, N_{k'-1}, N_{k'} - 1, N_{k'+1}, \dots, N_{max}) \ c^*(N_1, N_2, \dots, N_{k-1}, N_k - 1, N_{k+1}, \dots, N_{max}) \quad (9)$$

and

$$|A(k, \mathbf{m})\rangle = \frac{2\pi i}{\hbar} \varepsilon(N_k, \omega_k) |E_k, \mathbf{m}\rangle \langle E_k, \mathbf{m} | \hat{\epsilon} \cdot \mathbf{d} | E_i \rangle \quad (10)$$

If  $t_0$  denotes the time at which the pulse is over then, given Eq. (8), the molecule will evolve after  $t_0$  as

$$\begin{aligned} \rho_{mol}(t > t_0) = & \sum_{\mathbf{N}, \mathbf{m}, \mathbf{m}', k} |c(\mathbf{N})|^2 |A(k, \mathbf{m})\rangle \langle A(k, \mathbf{m}')| \\ & + 2 \sum_{\mathbf{N}, \mathbf{m}, \mathbf{m}', k' > k} \text{Re}[d_{k', k} |A(k, \mathbf{m})\rangle \langle A(k', \mathbf{m}')| \exp[-i(E_k - E_{k'})(t - t_0)/\hbar]] \end{aligned} \quad (11)$$

For example, for coherent states the real, positive  $d_{k, k'}$  can be composed from Eq. (4).

It is clear from these result that one photon absorption from the coherent pulse of light excites many material states, producing a *coherent molecular superposition state* that evolves in time. The energy of this superposition state, which is composed of many  $|E_k, \mathbf{m}\rangle$  eigenstates, is not sharply defined. Therefore, until we make some energy measurement we have no knowledge of the mode from which the photon was absorbed. This uncertainty in the absorbed energy is intimately tied to the fact that the system evolves in time after light absorption. This, in turn, arises from the fact that  $|R_i\rangle$  is itself a superposition of states of the radiation field.

Consider now absorption of light emitted by an incoherent thermal source, such as sunlight. This source consists of a statistical mixture of number states described by a radiation field density matrix<sup>10</sup>:

$$\rho_R = \sum_{\mathbf{N}} p_{\mathbf{N}} |\mathbf{N}\rangle \langle \mathbf{N}|. \quad (12)$$

Here  $p_{\mathbf{N}}$  is the probability of finding the number state  $|\mathbf{N}\rangle$  in the radiation emitted from the thermal source. If the source is at temperature  $T$  this is given by:

$$p_{\mathbf{N}} = \prod_k \frac{(\overline{N}_k)^{N_k}}{(1 + \overline{N}_k)^{1+N_k}} \quad (13)$$

with  $\overline{N}_k$  being the mean number of photons at temperature  $T$ :  $\overline{N}_k = [\exp(\hbar\omega_k/k_B T) - 1]^{-1}$ . This radiation field is a statistical mixture of number states. As a consequences, irradiation with this source will yield the result of an uncorrelated collection of states resulting from excitation with the state  $|\mathbf{N}\rangle \langle \mathbf{N}|$ .

Excitation with the state  $|\mathbf{N}\rangle \langle \mathbf{N}|$  would arise from the above treatment, with  $c(\mathbf{N}) = 1$  in Eq. (2). In this case, in Eq. (9)  $d_{k, k'} = \delta_{k, k'}$  and Eq. (8) becomes

$$\rho_{mol} = \sum_{\mathbf{m}, \mathbf{m}'} |A(k, \mathbf{m})\rangle \langle A(k, \mathbf{m}')| \quad (14)$$

Hence, the result of excitation with radiation emitted by a thermal incoherent CW source is that the system is in a mixture of stationary states.

The results of the above analysis are clear, but a discussion is warranted. Absorption of one photon from a coherent pulse creates a superposition of energy eigenstates, and hence a time evolving state. By contrast, absorption from a thermal incoherent CW source, creates a stationary mixture. The results of this quantized-radiation field analysis of one photon absorption is in agreement with that previously obtained<sup>7</sup> in the treatment of state preparation in an ensemble of molecules irradiated by either coherent or incoherent classical light. What is clearer here, however, is the specific focus on the absorption of a single photon. This analysis can now be used to comment on the associated physics and on current concerns that have arisen regarding one-photon absorption.

Recent qualitative considerations have led to incorrect conclusions, such as that the coherence of the molecule is independent of the nature of the source. Related incorrect pictures have also arisen, suggesting, for example, that each incident photon in weak CW light gives the molecule “a kick”, which induces dynamics in the molecule. These views, not supported by the above analysis, arise from a simplistic particle picture of the photon<sup>16</sup>, and are dispelled when one appreciates the role of measurement in quantum mechanical particle/wave duality. That is, as is typically the case, whether a system behaves like a wave or a particle depends upon the nature of the measurement<sup>17</sup>. For example, in the case of pulsed light absorption described above, no measurement is made that would reveal particle-like properties of the photon. Hence, utilizing a particle picture is not correct for this physical scenario.

Similarly, for the pulse case, were one to undertake an experiment in which measurements of the energy of the molecule subsequent to absorption of light from a pulse were made, then stationary states at fixed energy would emerge. Such a measurement is not done, and hence the energy of the system is uncertain, which is intimately related to the fact that the molecule undergoes time evolution. By contrast, a thermal source, by its very nature, is comprised of independent fixed energy photons and, as such, creates stationary molecular states upon irradiation. That is, conservation of energy ensures that an initial energy eigenstate, absorbing a single photon of known energy, reaches a stationary excited state with known energy, and no time evolution.

Similarly, the classical picture of the photon as a particle incident on the molecule, possessing only information about its energy and polarization, and possessing no characteristics associated with the source of the radiation, is incorrect. Specifically, as is evident from the analysis above, the effect that the photon has on the molecule depends intimately on the

nature of the light source. Multimode coherent pulses induce dynamics whereas CW sources (and likewise natural thermal sources) do not.

The classical picture of the photon as a particle incident on the molecule, repeatedly initiating dynamics, also assumes a known photon arrival time. This too is incorrect and inconsistent with the quantum analysis insofar as no specific arrival time can be presumed unless the experiment itself is designed to measure such times.

Finally, as is well-known, even thermal sources will create *short time* initial coherences associated with the initial time that the molecule feels the turn-on of the light<sup>11,18</sup>. Short time dynamics is then manifest. However, under natural circumstances (such as moonlight<sup>3</sup> or sunlight) such initial time evolution is totally irrelevant on the timescales associated with natural light<sup>3</sup>.

Finally, suggestions have been made that a thermal source may be regarded as a collection of random femtosecond pulses<sup>1</sup>. As such, the suggestion goes, each molecule feels the effect of individual femtosecond pulses and as such, undergoes coherent time-dependent evolution. This perspective is also unjustified. That is, the electric field from a thermal light source can be expanded in a variety of different bases. However, it is the *overall* effect of the light that is important, and this overall effect is to populate energy eigenstates of the molecule. There is no justification for imposing a physical picture associated with femtosecond pulses on the natural process if the natural scenario makes no such measurement.

In summary, the above approach makes clear the extent to which quantum mechanics allows a physical picture of one photon absorption in an isolated molecule. An analogous picture arises in open systems<sup>13</sup>. Any additional imposed qualitative picture may well be inconsistent with quantum mechanics.

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